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PERTURBED γ - γ DIRECTIONAL CORRELATIONS AND THE COMPLEX CHEMISTRY OF HAFNIUM AND TANTALUM

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Abstract—In the experiments described in this paper, the γ - γ directional correlation in the decay of ^{181}Hf was measured in dilute aqueous solutions containing varying amounts of fluoride. The observed variations in the anisotropy are explained from complex formation and precipitation, possibly preceded by polymerization. The results indicate that measurements of directional correlations may provide a useful tool for studies of complex formation in dilute solutions of suitable elements.

INTRODUCTION

It is generally accepted in radiochemistry that nuclear properties are independent of the chemical form in which radioactive atoms are present. Exceptions are the half-lives of some isotopes decaying through internal conversion or capture of the outer electrons and the directional correlations between consecutively emitted particles or photons. The influence of the chemical and physical surrounding of a decaying nucleus on directional correlations has been measured by a number of investigators[1]. In most comparative studies of radioactive compounds in solutions both the chemical form of the decaying atoms and the physical properties of the solutions were varied[2, 3]. The form reported in this paper was carried out in order to investigate the relation between the observed γ - γ directional correlation and the chemical form of radioactive atoms in physically identical aqueous solutions and to evaluate the possible application of these measurements in chemistry research.

The directional correlation measurements were applied to the (133 + 137)–482 keV γ - γ cascade in the decay of ^{181}Hf . The choice of this isotope was based partly on the favourable physical properties of the daughter ^{181}Ta for perturbed directional correlation studies and partly on the existence of stable HF-fluoride complexes formed after addition of only minor amounts of fluoride to acid Hf-solutions[4], without changing essentially the physical properties of these solutions.

PERTURBED γ - γ DIRECTIONAL CORRELATIONS IN THE DECAY OF ^{181}Hf

When in the decay of a nucleus two γ -rays are emitted successively, the probability of the emission of the second γ -ray under an angle θ with respect to the direction of the first γ -ray, is given by:

$$W(\theta) = 1 + A_1 P_2(\cos \theta) + A_4 P_4(\cos \theta),$$

where θ = angle between the directions of the successive γ -rays, A_2, A_4 = directional correlation coefficients, these are constants for a given cascade, $P_2(\cos \theta), P_4(\cos \theta)$ = Legendre-polynomials.

This relation is only valid under the restriction that the orientations of the spins of the decaying nuclei do not change during the lifetime of the intermediate state after

the emission of the first γ -ray. In general, the observed anisotropy is weakened due to interactions of the nuclear magnetic dipole moment of the intermediate state with local magnetic fields or interactions of the nuclear electric quadrupole moment of the intermediate state with local electric field gradients. For the electric interactions, the extent of the perturbation depends on the mean life of the intermediate state, on its electric quadrupole moment and on the local electric field gradient. The observed perturbed directional correlation, when the time-resolution of the coincidence circuit is large compared with the mean life of the intermediate state, is given by:

$$W(\theta) = 1 + G_2 A_2 P_2(\cos \theta) + G_4 A_4 P_4(\cos \theta)$$

where G_2, G_4 = time integrated attenuation factors.

In the experiments described in this paper we have measured the time integrated attenuation factors of the directional correlations of the (133 + 137)–482 keV γ - γ cascade in the decay of ^{181}Hf (Fig. 1). Since both the mean life and the quadrupole moment of the intermediate 482 keV state are relatively large—15.3 ns and 2.5 b respectively[5, 6]—strong perturbations may occur. So measurements of these directional correlations can be expected to provide a sensitive way of observing changes in the molecular or ionic structure of Hf-compounds accompanied by changes in the internal electric fields.

An extra possibility for obtaining information about physico-chemical properties of Hf and Ta is offered by the long mean life (25.4 μs) of the intermediate level between the initial β -transition and the γ - γ cascade actually occurring in the ^{181}Ta nucleus. It makes possible a measurement of the perturbation of the directional correlation at different delay times after the transition of a Hf into a Ta atom. If this type of measurement is applied to suitable solutions in which the chemical forms of the Hf- and Ta-compounds are different, information about molecular reaction rates on a 5–50 μs time scale will in principle be obtained.

EXPERIMENTAL

Sources

The γ - γ directional correlation experiments were carried out with 1 ml ^{181}Hf -sources sealed in small polyethylene capsules. Stock solutions were prepared of reactor irradiated HfOCl_2 in 1.0

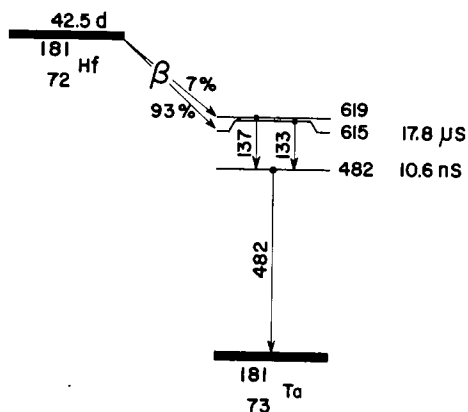


Fig. 1. The relevant part of the decay scheme of ^{181}Hf .

and 0.1 N HClO_4 . Sources with different fluoride concentration were obtained by addition of weighed amounts of NaF to aliquots of the stock solutions pipetted into the capsules.

The results described in this paper were obtained by measuring two series of sources with the following compositions:

| | | |
|-----------|-----------------------------|--------------------------------|
| Series A: | Hf-concentration | 5 mg/ml |
| | spec. activity | 1 mCi/g |
| | solvent | 1.0 N HClO_4 in water |
| | F^- -concentration | 0–10 mg/ml |
| Series B: | Hf-concentration | 0.4 mg/ml |
| | spec. activity | 8 mCi/g |
| | solvent | 0.1 N HClO_4 in water |
| | F^- -concentration | 0–10 mg/ml |

Each source was prepared individually and the measurements were started within 5 min after source preparation. The γ - γ directional correlations as function of delay after the β -transition have been measured with a source containing 0.5 mg hafnium and 4 mg fluoride per ml.

Measurement of γ - γ directional correlations

The automated γ - γ directional correlation measuring system used in these experiments consists of two $3'' \times 3''$ NaI(Tl)-detectors connected to a coincidence system. The source-detector distance was 8 cm and the coincidence resolving time 50 ns. The counting sequence consisted of blocks of measurements with $\theta = \frac{1}{2}\pi, \frac{3}{4}\pi, \pi, \frac{5}{4}\pi$ and $\frac{3}{2}\pi$; the counting time in each position was 200 or 400 s. The results, consisting of numbers of coincidence, chance coincidence and single counts were put on punched tape. The values for G_2A_2 and G_4A_4 were calculated using a DEC PDP-9 computer after appropriate correction for chance coincidence, decay and geometric attenuation.

Measurement of γ - γ directional correlations as function of delay after the β -transition

For these measurements approx. 10 μl of the sample solution was put into a small hole in a cylindrical piece of a plastic scintillator, optically coupled to a photomultiplier tube (Fig. 2). In this setup the plastic scintillator is used both as source holder and as β -ray detector. The plastic scintillator was placed in the γ - γ

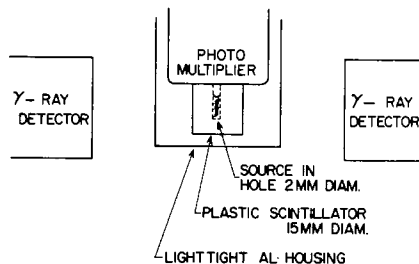


Fig. 2. Experimental setup used in the measurement of γ - γ directional correlations as function of delay after β -transition.

directional correlation system described above. The signals from the β -ray detector were combined with the signals from the γ - γ coincidence system in a slow coincidence circuit with selectable resolving and delay time. The counting time in each position was 15 min. The total measuring time was 4 weeks.

RESULTS AND DISCUSSION

γ - γ Directional correlations

Figures 3 and 4 show the values for G_2A_2 and G_4A_4 found when measuring the two series of samples. For both series, a sharp increase of $|G_2A_2|$ —and $|G_4A_4|$ —is observed when only small amounts of fluoride are added to the solutions. The maximum values for $|G_2A_2|$, particularly for samples with low Hf-concentration, are reasonably close to the theoretical unperturbed value -0.2919 for A_2 of the measured transitions. Further increase of the F^- -content results in a strong decrease of $|G_2A_2|$, which coincides with a partial colloidal precipitation. A striking effect is observed for the dilute Hf-solutions containing 3–5 mg F^-/ml . For these samples, the value of $|G_2A_2|$ measured short after addition of the fluoride is high but decreases as a function of time until a constant equilibrium value is reached (Fig. 5). The equilibrium value and the time required to reach this value

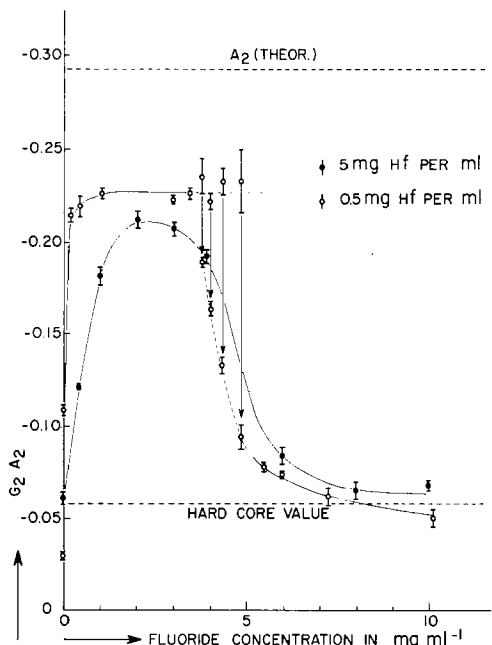


Fig. 3. G_2A_2 for sources containing different amounts of fluoride.

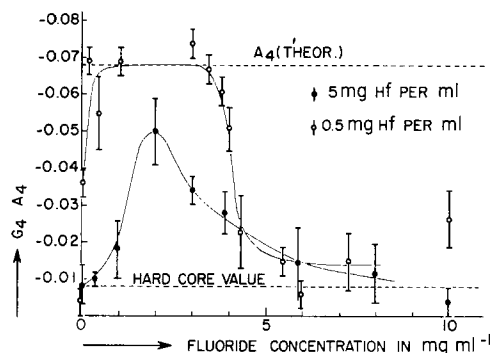


Fig. 4. G_4A_4 for sources containing different amounts of fluoride.

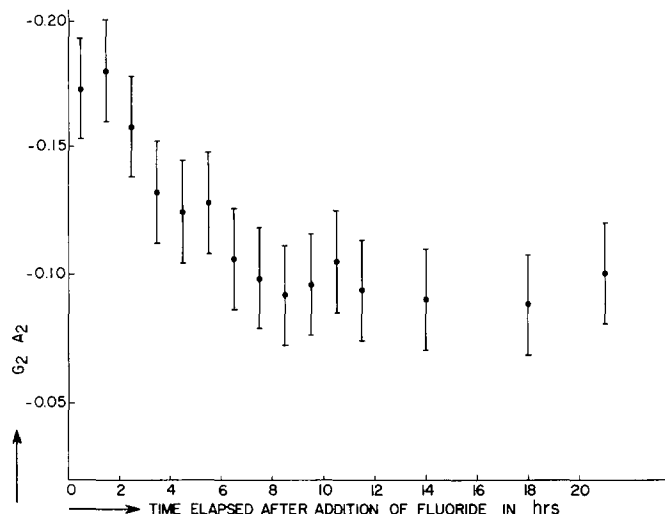


Fig. 5. G_2A_2 as function of time elapsed after addition of 4.8 mg fluoride per ml to a solution containing 0.5 mg hafnium per ml.

strongly depend on the F^- -concentration; the latter ranges from tens of hours for 4 mg F^- /ml to tens of minutes for 5 mg F^- /ml. In Fig. 3, points representing initial and final values are connected by an arrow.

The first parts of the curves, for F^- -concentrations up to 3 mg/ml, could represent the formation of HfF -complexes from the $Hf(OH)$ -complexes present in fluoride-free solutions. This interpretation gets some support when the values for G_2A_2 are plotted as a function of the ratio of F^- and Hf -atoms present in the samples (Fig. 6). In this figure, at low atomic ratios, the two series can be represented by one curve and for both series maximum values for $|G_2A_2|$ are reached for atomic ratios $F/Hf \approx 6$. Obviously, a surrounding of Hf -atoms with six or more F -atoms strongly reduces the internal field gradients, resulting in an almost unperturbed directional correlation.

The increase of the perturbation for F^- -concentrations exceeding 3 mg/ml is in agreement with the observed formation of a precipitate but the long time constants of the changes of the directional correlation measured after addition of fluoride are rather surprising. Some insight in the type of reactions possibly preceding or accompanying the precipitation can be obtained from a plot of the inversed time constant of the change of the anisotropy versus the free fluoride concentration (Fig. 7). As a first approximation, the free fluoride concentration is calcu-

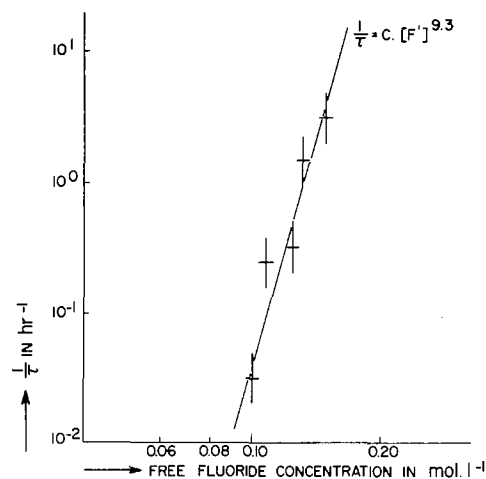
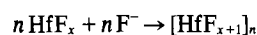


Fig. 7. Reaction time constant as function of the free fluoride concentration.

lated as the total amount of fluoride present minus the amount of fluoride equivalent to the amount of $HClO_4$ present in the samples. The time constants τ are calculated by fitting an exponential function

$$A_2G_2(t) = A_2G_2(0) e^{-t/\tau} + A_2G_2(\infty)$$

to the values for G_2A_2 as measured at different waiting times t after addition of fluoride to the solutions. The high power relation between $1/\tau$ and F^- -concentration indicates that the reactions are at least of high order with respect to fluoride. This seems to point to a polymerization reaction



as part of the precipitation mechanism and supports the reported formation of polymers of hafnium and chemically related elements in aqueous solutions [7, 8] and in solids [9, 10]. The values of approx. -0.07 and -0.01 for G_2A_2 and G_4A_4 measured at high fluoride concentrations agree very well with the theoretical hard core values—

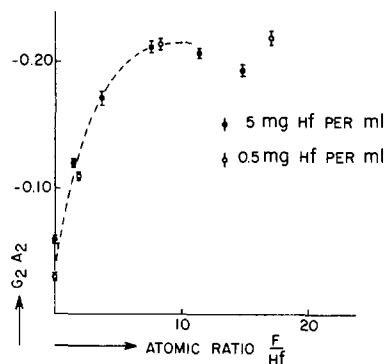


Fig. 6. G_2A_2 as function of the ratio of F^- and Hf -atoms present in the source.

−0.058 and −0.0076—for perturbation in a static axially symmetric field gradient in a solid.

γ-γ Directional correlations as function of delay after β-transition

The results of this experiment are shown in Table 1,

Table 1. Directional correlations at different intervals $t_i - t_f$ after β-emission

| t_i (μs) | t_f (μs) | G_2A_2 |
|------------|------------|--------------------|
| 0 | ∞ | -0.102 ± 0.010 |
| 3.4 | 11.9 | -0.104 ± 0.037 |
| 29.4 | 47.9 | -0.103 ± 0.043 |

where G_2A_2 is given as a function of the delay $t_f - t_i$ with respect to the initial β-transition. From this table it can be concluded that for delays of 5–50 μs, the anisotropy is within the experimental errors independent of the time elapsed after the β-transition.

This result can be explained in three different ways:

(a) the adaption of the chemical surrounding of a newly formed Ta-atom from a Hf-atom takes place in less than 5 μs or considerably more than 50 μs;

(b) the change of the chemical form does not affect the observed γ-γ directional correlation;

(c) there is no significant difference between the chemical forms of hafnium and tantalum in the solution used in this experiment.

On the basis of present knowledge it seems impossible to choose between these three alternatives. An extensive study of the halocomplexes of hafnium and tantalum and many coincidence measurements are required in order to reach a conclusion with respect to the value of this type of directional correlation measurements in studies of chemical transformations on short time scales.

CONCLUSIONS

The results of the experiments described in this paper show that measurements of perturbed directional correla-

tions can be used for monitoring chemical reactions in solutions. Although the measuring technique is rather complicated and time-consuming and only applicable to a limited number of isotopes with appropriate decay schemes, it can be very useful in studies of very dilute solutions to which experimental methods commonly used in inorganic chemistry research cannot be applied. When using radioactive preparations of high specific activity, directional correlation measurements can be applied to solutions containing only nanogram amounts of the element under study. Moreover, there are no requirements with respect to the containment of the samples as long as most of the emitted γ-rays can pass through the container walls. This can be an advantage over optical methods in studies of solutions to which quartz cuvettes are not resistant, i.e. acid fluoride solutions.

The results of the measurements of γ-γ directional correlations as a function of delay after β-transition, as described in this paper, only prove that this type of measurements is possible without excessive technical problems. In our opinion however, these time dependent measurements seem to offer the possibility of monitoring reactions on a microsecond time scale.

REFERENCES

1. E. Karlsson, E. Matthias and K. Siegbahn, *Perturbed Angular Correlations*. North-Holland, Amsterdam (1964).
2. R. M. Steffen, *Phys. Rev.* **103**, 116 (1956).
3. M. Forker, H. F. Wagner and E. Bodenstein, *Nucl. Phys.* **A138**, 644 (1969).
4. L. G. Sillen, *Stability Constants of Metal-Ion Complexes*. The Chemical Society, London (1964).
5. Y. A. Ellis, *Nuclear Data Sheets* **9**, 319 (1973).
6. R. W. Sommerfeldt, T. W. Cannon, L. W. Coleman and L. Schichter, *Phys. Rev.* **138**, 4B, 763 (1965).
7. R. S. Tobias and S. Young Tyree, *J. Am. Chem. Soc.* **81**, 6385 (1959).
8. G. M. Muka and P. A. Vaughan, *J. Chem. Phys.* **33**, 194 (1960).
9. J. C. Bailer, *Comprehensive Inorganic Chemistry*, p. 444. Pergamon Press, New York (1973).
10. R. B. King, *Progr. Inorg. Chem.* **15**, 287 (1972).